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Magnetic and Structural Study of the Spinel $MnYb_2S_4$

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P. M. Raccah

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LINCOLN LABORATORY

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Group 83

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ABSTRACT

The compound $MnYb_2S_4$ has the normal spinel structure with no measurable mixing of atoms in octahedral and tetrahedral sites. The sulfur parameter is 0.380 ± 0.002, which is lower than usually found in spinels. Magnetic susceptibility shows no magnetic order to liquid He temperature and a temperature dependence that is the simple sum of the theoretical contributions for Yb^{3+} and Mn^{2+} ions.

Accepted for the Air Force
Franklin C. Hudson
Chief, Lincoln Laboratory Office

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I. INTRODUCTION

Many compounds with the spinel structure are magnetic and therefore provide information about the signs and strengths of the interactions between magnetic ions. Previous studies of these interactions have been confined to transition-metal compounds with the spinel structure. Recently, rare-earth sulfur and selenium compounds with the spinel structure have been found. The rare-earth ions are on octahedral sites, and either a magnetic transition-metal ion or a nonmagnetic ion is on the tetrahedral sites. Suchow and Stemple[1] have prepared various rare-earth spinels having cadmium ions on the tetrahedral sites. Patrie, Flahaut, and Domange[2] have studied rare-earth thiospinels having iron, manganese, or magnesium on the tetrahedral sites. These systems provide an opportunity to study the signs and magnitudes of the interactions between the rare-earth ions and between the rare-earth and transition-metal ions. Since interactions between octahedral-site ions in spinels are, in general, relatively weak, this study represents an investigation of the magnetic interactions between an octahedral-site Yb^{3+} ion and a tetrahedral-site Mn^{2+} ion in the thiospinel $MnYb_2S_4$. Since these interactions are mediated via covalent mixing with the anions it was anticipated that the greater covalency of sulfur, relative to oxygen, would enhance the magnitude of their interactions.

II. EXPERIMENTAL

$MnYb_2S_4$ was first prepared as described by Patrie, et al.[2] This involves heating a stoichiometric mixture of the oxides in a stream of H_2S at about 1300°C. However, a more reproducible product was prepared by heating at 1300°C for 24 hrs. a stoichiometric mixture of ytterbium sulfide, manganese metal, and sulfur in an aluminum crucible that had been sealed under vacuum in a silicon tube. The samples were microcrystalline and olive-green in color. They had a face-centered-cubic unit cell with $a = 10.95$ Å, which is in agreement with Patrie, et al.

The magnetic susceptibility χ of a 0.1312 gram sample was measured in a field of 10 kOe from liquid He to room temperature with a vibrating-sample magnetometer developed at this laboratory.[3] The $1/\chi$ vs T plot is shown in Fig. 1. At higher temperatures the curve obeys a Curie-Weiss law

$$\chi_m = C_m/(T - \Theta_p) \qquad (1)$$

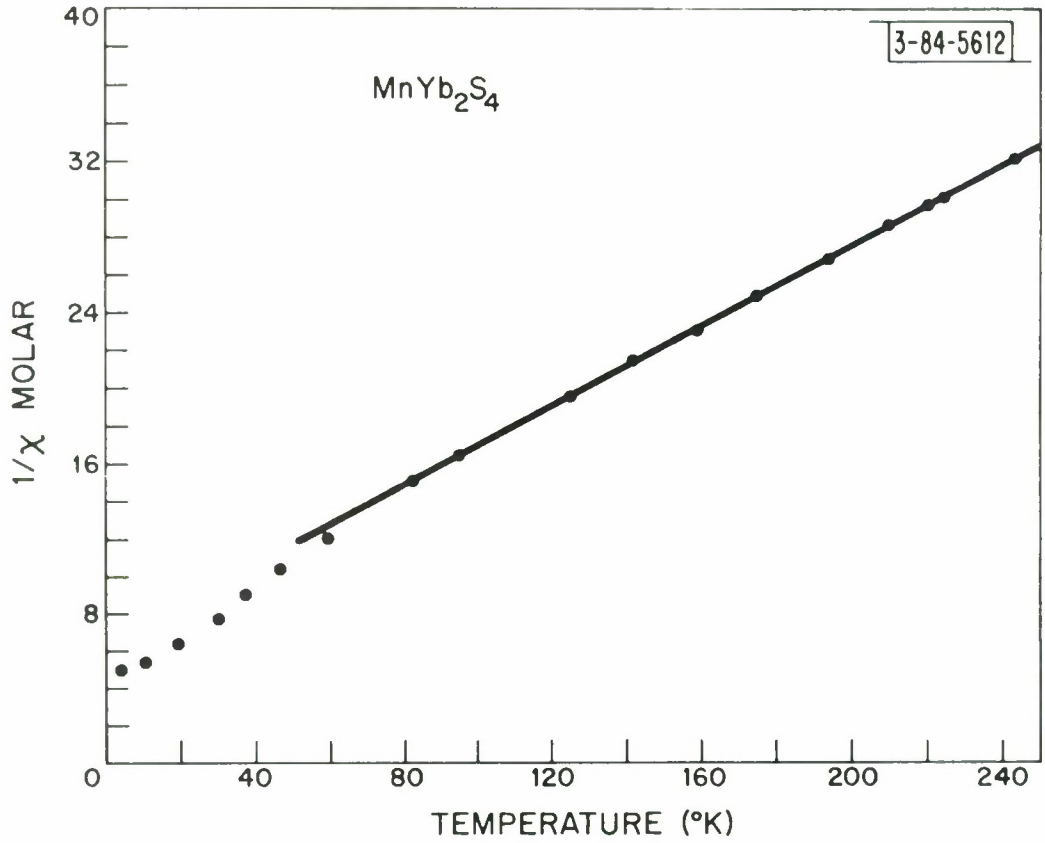

Fig. 1. Inverse molar susceptibility vs temperature for $MnYb_2S_4$.

with molar Curie constant $C_m = C(Yb) + C(Mn) = 9.52$. Theoretical and experimental values for the contribution of the two ytterbium ions to C_m are[4] $C(Yb) = 2 \times 2.58 = 5.16$. This leaves a $C(Mn) = 4.36$, which corresponds to a $n_{eff}^{Mn} = \sqrt{8C(Mn)} = \sqrt{34.9}$. The theoretical value for Mn^{2+} ions is $n_{eff}^{Mn} = g\sqrt{S(S+1)} = \sqrt{35}$. Magnetization vs magnetic field at both liquid N_2 and liquid He temperatures showed a linear dependence, characteristic of the paramagnetic state.

The relative x-ray diffraction intensities of a finely ground powder which passed a 325 sieve were measured with a General Electric X-RD5 diffractometer using Ni filtered Cuk$_\alpha$ radiation. In order to eliminate the long-term drift of the instrument, the intensity of every peak is expressed relative to the strongest peak (311), which was remeasured each time. Where two peaks could not easily be separated, their intensities are grouped into a single intensity. The structural parameters were refined with the aid of a computer program developed at this laboratory[5] that is able to adjust all positional parameters, isotropic temperature factors, and site occupancies to obtain a minimum value for the factor R defined as

$$R \equiv \frac{\sum_{hk\ell} \left| I_{obs}(hk\ell) - I_{calc}(hk\ell) \right|}{\sum_{hk\ell} I_{obs}(hk\ell)} \times 100 \quad .$$

In the refinement, the theoretical form factors (Mn^{2+}, Yb^{3+}, S^0) used were those calculated by Cromer and Waber.[6] Both the real and the imaginary parts of the anomalous-dispersion correction, as calculated by Cromer,[7] were applied. Comparison of observed and calculated intensities is presented in Table I.

III. DISCUSSION

The magnetic-susceptibility data can be accounted for nicely by simple paramagnetism with so little interaction between the ions that there is no long-range magnetic order at liquid He temperature. The bend in the $1/\chi$ vs T plot at very low temperatures is similar to that found in YbF_3[4] and is therefore attributed to the Yb^{3+} ions. Subtraction of the ytterbium contribution leaves a straight line with a slope corresponding to the theoretical Mn^{2+} contribution.

The final refinement of parameters had an R = 8.2. It gave a sulfur $\underline{u}$ parameter of 0.380 ± 0.002 and the isotropic temperature factors $B_{Mn} = 0.03$, $B_{Yb} = 0.54$, $B_S = 0.07$. Patrie, et al.[2] have reported a $\underline{u} = 0.375 \pm 0.004$. However, their result was based only on the ratio of intensities of two sets of

TABLE I

X-RAY POWDER DATA FOR $MnYb_2S_4$

$\underline{a}$ = 10.95 Å, R = 8.2, $\underline{u}$ = 0.380, λ = 1.5418 Å

I-OBS	I-CAL	TWO THETA	H	K	L	I-OBS	I-CAL	TWO THETA	H	K	L
64.2	64.2	14.00	1	1	1	6.6	4.5	79.72	7	5	3, 9 1 1
8.9	5.7	22.95	2	2	0	8.0	7.4	84.30	9	3	1
100.0	100.0	26.99	3	1	1	23.6	22.6	87.15	8	4	4
27.2	26.5	28.21	2	2	2			88.85	7	5	5, 9 3 3,
									7	7	1
50.2	63.2	32.69	4	0	0	11.8	11.9	91.68	8	6	2, 10 2 0
16.2	15.8	35.71	3	3	1			93.39	7	7	3, 9 5 1
4.9	2.5	40.32	4	2	2			93.96	6	6	6, 10 2 2
44.2	41.0	42.88	5	1	1, 3 3 3	2.9	2.4	97.95	9	5	3
63.4	69.6	46.90	4	4	0	4.1	3.5	102.56	7	7	5, 11 1 1
15.8	15.9	49.19	5	3	1	11.9	10.9	105.48	8	8	0
3.1	1.0	52.84	6	2	0			107.26	9	5	5, 9 7 1,
									11	3	1
24.8	25.3	54.94	5	3	3	10.8	8.4	112.07	9	7	3, 11 3 3
		55.63	6	2	2			112.69	10	6	2
16.2	14.0	58.34	4	4	4	11.7	11.7	115.17	8	8	4, 12 0 0
9.0	8.2	60.32	5	5	1, 7 1 1			117.06	7	7	7, 11 5 1
2.0	1.2	63.53	6	4	2	8.4	8.1	122.29	9	7	5, 11 5 3
19.2	20.4	65.42	5	5	5, 7 3 1	15.9	15.9	125.78	12	4	0
								127.83	9	9	1
8.8	9.9	68.50	8	0	0	12.0	13.3	133.83	11	5	5, 13 1 1
2.3	1.4	70.32	7	3	3				11	7	1, 9 9 3
1.0	.6	73.30	8	2	2, 6 6 0			134.62	10	6	6
14.8	15.2	75.07	5	5	5, 7 5 1	11.6	14.4	137.91	12	4	4
		75.66	6	6	2			140.51	11	7	3, 9 9 3
									13	3	1
17.0	16.2	77.99	8	4	0						

reflections: 311/333-511 and 531/731-533. The relatively low value of the $\underline{u}$ parameter in this manganese spinel ($MnIn_2S_4$ has $\underline{u} = 0.384$ and $MnCr_2S_4$ has $\underline{u} = 0.3863$[8]) is due to the larger size of Yb^{3+} relative to Cr^{3+} or In^{3+}.

In the spinel $MnYb_2S_4$, the Mn^{2+} ions occupy tetrahedral sites and the Yb^{3+} ions occupy octahedral sites. For ideal close packing of the sulfur ions, $\underline{u} = 0.375$. In general a $\underline{u} > 0.375$ is found in cubic spinels. Several attempts were made to reduce the factor R below 8.2. First, a fraction of the Mn^{2+} and Yb^{3+} ions were allowed to interchange between octahedral and tetrahedral sites. This gave no improvement, as might have been expected from the site preferences of these ions. Second, some tetrahedral Mn^{2+} ions were allowed to move to empty, octahedral-site interstitial positions. This also gave no improvement. Finally, the concentration of sulfur was allowed to vary as a check for gross nonstoichiometry. The results showed each sulfur site having a concentration of 0.97 ± 0.05, with no significant lowering of the R factor. It is believed that a lower R factor was not attained because of surface attack of the sample by the atmosphere.

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